

# Evaluation of Volatile Species in Green Monopropellant Project

Center Independent Research & Developments: JSC IRAD Program | Mission Support Directorate (MSD)



## ABSTRACT

NASA is interested in green monopropellants to replace hydrazine in reaction control systems (RCSs). Some current NASA programs require reduced vapor pressure and low toxicity monopropellant (green) and superior performance (specific impulse and density) formulations. Earlier vapor phase studies of a candidate green monopropellant at the NASA White Sands Test Facility (WSTF) showed the presence of a volatile species that warranted further investigation. The purpose of this study was to further characterize the volatile species and to evaluate it. The evaluation was with respect to whether the volatile species was an impurity or how it is formed, and to use that information to examine whether its presence as an impurity can be eliminated during formulation. The evaluation also considered whether formation of the volatile impurity could be prevented while not compromising the propellant. To reduce variables associated with evaluation of the propellant formulation as a whole, a precursor to one of the individual components in the propellant formulation was subjected to a NASA Standard 6001B Flammability, Offgassing, and Compatibility Requirements and Test Procedures "Determination of Offgassed Products (Test 7)". Testing took place in the NASA WSTF Molecular Desorption and Analysis Laboratory. One gram of the precursor was placed in a flask within a specimen container. After thermal conditioning for  $72 \pm 1$  h at  $50 \pm 3$  °C ( $122 \pm 5$  °F), the atmosphere inside the specimen container was analyzed for offgassed compounds by cryotrap gas chromatography-mass spectrometry (GC-MS) and fixed sample loop GC-flame ionization detection (GC-FID). The specimen container used was glass to minimize potential catalytic surfaces. The identification of compounds was difficult due to the complexity of the vapor phase concentrations and overlapping chromatographic peaks and mass spectra.

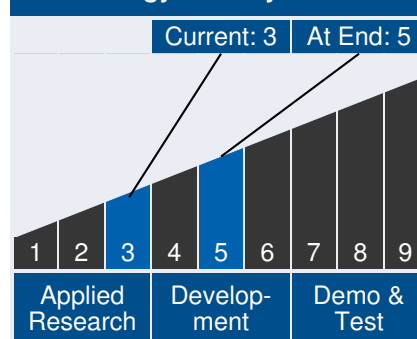


Green Propulsion Module

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## Technology Maturity



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However, eleven compounds were specifically identified and five compounds or classes of compounds were reported as unidentified. Quantitation of most of the compounds, including unidentified compounds, was as methane. Quantitating compounds or classes of compounds that were detected but for which specific calibration is not established as methane is in accordance with the Test 7 standard protocol. The thermal decomposition temperature of the precursor was significantly higher than the test temperature. Based on thermal decomposition temperature and on an examination of the structure and chemistry of the identified volatile species, the presence of the volatile species appears to be chemically reasonable with respect to the propellant formulation and is at this time attributed to impurities. Further examination of the overall propellant formulation process (including the individual components' synthesis processes) and process quality control (including purity of reagents and possible decomposition reactions) is indicated.

## ANTICIPATED BENEFITS

### To NASA funded missions:

This work may provide a better understanding of green propellants and reduce or eliminate problems as they pertain to NASA funded missions. Improved understanding of the volatile species will help to achieve performance targets of improved handling and non-toxicity benefits. Otherwise, campaign costs can increase because increased levels of personnel safety may be required. In addition, if risk is not mitigated, schedule may be delayed because of ground operations safety assessments, development and implementation of corresponding engineering controls, and selection and use of personal protective equipment. These in turn affect ground operations and can extend vehicle/flight readiness, storage and loading operations,



1 New Technology Report

### Management Team

**Program Director:**

- Douglas Terrier

**Program Executive:**

- Douglas Terrier

**Program Manager:**

- Douglas Terrier

**Project Manager:**

- Ronald Clayton

**Principal Investigator:**

- Benjamin Greene

**Co-Investigators:**

- Dion Mast
- Mark McClure

### Technology Areas

**Primary Technology Area:**

In-Space Propulsion Technologies (TA 2)

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and decontamination/cleaning operational times.

## **To NASA unfunded & planned missions:**

Similar to the benefits of NASA funded missions, this work may provide a better understanding of green propellants and reduce or eliminate problems as they pertain to NASA funded missions. Improved understanding of the volatile species will help to achieve performance targets of improved handling and non-toxicity benefits. Otherwise, campaign costs can increase because increased levels of personnel safety may be required. In addition, if risk is not mitigated, schedule may be delayed because of ground operations safety assessments, development and implementation of corresponding engineering controls, and selection and use of personal protective equipment. These in turn affect ground operations and can extend vehicle/flight readiness, storage and loading operations, and decontamination/cleaning operational times.

## **To other government agencies:**

Other government agencies that use, test, provide, or partner with NASA on green monopropellants may gain the same benefits as NASA.

## **To the commercial space industry:**

The commercial space industry that is marketing or using green monopropellants will gain insight into NASA's interests and experience.

## **To the nation:**

As NASA and other government agencies gain benefits, industry may gain similar benefits. Overall, increased performance and improved safety will benefit space missions and provide the nation with higher performance and lower cost space initiatives.

## **DETAILED DESCRIPTION**

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This project investigated the formation of a volatile species in a candidate green monopropellant alternative to hydrazine. A single compound that is a precursor to an ingredient in the monopropellant formulation was tested.

NASA is interested in green monopropellants to replace hydrazine in reaction control systems (RCSs). RCSs are used to maneuver spacecraft in orbit. Current and projected programs require reduced vapor pressure and low toxicity monopropellant (green) and superior performance (specific impulse and density) formulations. Earlier vapor phase studies of a candidate green



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monopropellant at the NASA White Sands Test Facility (WSTF) showed the presence of a volatile species that warranted further investigation. The purpose of this study was to further characterize the volatile species and to evaluate it. The evaluation was with respect to whether the volatile species was an impurity or how it is formed, and to use that information to examine whether its presence as an impurity can be eliminated during formulation. The evaluation also considered whether formation of the volatile impurity could be prevented while not compromising the propellant. Because the green monopropellant is a mixture of compounds, and to simplify the experiment by reducing variables, a single precursor to one of the individual components in the propellant formulation was selected for testing. The selection of the precursor as a test material was based on the relation of the precursor's structure to the volatile species. The selection also considered likely synthetic routes of the precursor's production that might introduce impurities due to incomplete yields or inadequate purification, and possible side reactions of these with other components in the green monopropellant formulation.

## **Experimental**

The precursor was obtained commercially at a stated concentration of greater than 98%, which was the highest purity available from an available manufacturer survey. An aliquot of the precursor was tested using NASA Standard 6001B *Flammability, Offgassing, and Compatibility Requirements and Test Procedures* "Determination of Offgassed Products (Test 7)". Testing was performed in the NASA WSTF Molecular Desorption and Analysis Laboratory. One gram of the precursor was placed in a flask within a specimen container that was used to develop and contain the vapors for analysis. After thermal conditioning for  $72 \pm 1$  h at  $50 \pm 3$  °C ( $122 \pm 5$  °F), the atmosphere inside the specimen container was analyzed for offgassed compounds by cryotrap gas chromatography-mass spectrometry (GC-MS) and fixed sample loop GC-flame ionization detection (GC-FID). Quantitation of compounds, including unidentified compounds, for which specific calibration factors did not exist, was as methane in accordance with the Test 7 standard protocol. The specimen container that was used was made of glass to minimize potential catalytic surfaces that might occur on metal surfaces.

## **Results and Discussion**

The test data were complex, and the identification of compounds was difficult because of widely varying vapor phase concentrations, overlapping chromatographic peaks, and overlapping mass spectra. Eleven compounds were specifically identified and five compounds or classes of compounds were reported as unidentified. Several compounds or classes of compounds did not

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have calibration factors, but were quantitated as methane in accordance with the Test 7 standard protocol. The qualitative nature of this investigation did not require exact concentrations.

An examination of the scientific literature indicated that the thermal decomposition temperature of the precursor was significantly higher than the test temperature. Also, the structure of the volatile species did not resemble a probable thermal decomposition products of the precursor. As the stated purity of the precursor was greater than 98% (which leaves allowances for impurities), we reason that the eleven compounds and five compounds or classes of compounds volatile species that were detected were impurities.

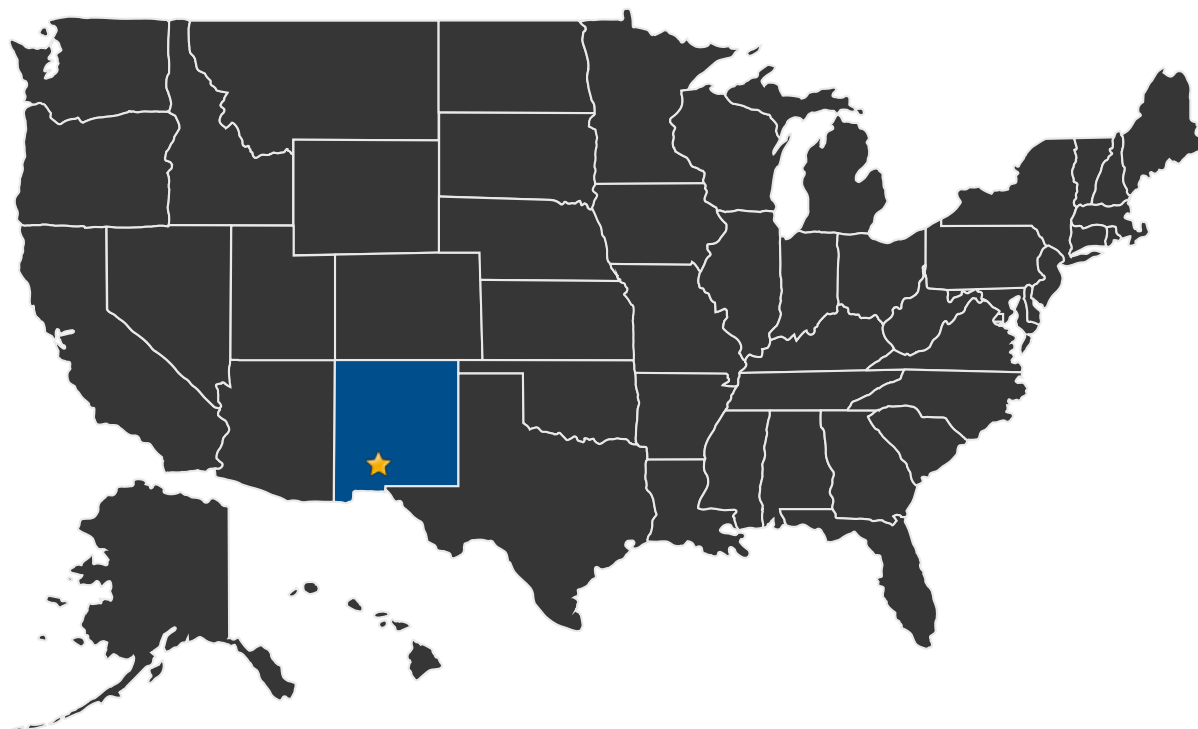
Further examination of the overall propellant formulation process (including the individual components' synthesis processes) and process quality control (including purity of reagents and possible decomposition reactions) is indicated.

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## U.S. LOCATIONS WORKING ON THIS PROJECT



■ U.S. States With Work

★ **Lead Center:**  
White Sands Test Facility

## PROJECT LIBRARY

### New Technology Reports

- Reduced Toxicity, High Performance Monopropellant at the U.S. Air Force

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## IMAGE GALLERY



*A Green Monopropellant Component Precursor in an Offgas Test Chamber*



*A Green Monopropellant in a Lab*



*Green Monopropellant Thruster Firing*



*Green Propellant Handling*



*Green Propellant Propulsion System*



*Hydrazine Thrusters*



*Not open safe?*



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## DETAILS FOR TECHNOLOGY 1

### Technology Title

Technological Advancement

### Technology Description

This technology is categorized as a material for other applications

The experimental technology is mature. NASA Standard 6001B *Flammability, Offgassing, and Compatibility Requirements and Test Procedures* "Determination of Offgassed Products (Test 7)" in the NASA WSTF Molecular Desorption and Analysis Laboratory was used to characterize volatile species in a precursor to a component of a green monopropellant alternative to hydrazine. A sample of the precursor was placed in a flask within a specimen container, and thermally conditioned for  $72 \pm 1$  h at  $50 \pm 3$  °C ( $122 \pm 5$  °F). The atmosphere inside the specimen container was then analyzed for offgassed compounds by cryotrap gas chromatography-mass spectrometry (GC-MS) and fixed sample loop GC-flame ionization detection (GC-FID). Eleven compounds were specifically identified and five compounds or classes of compounds were reported as unidentified. As the data were evaluated, the scientific literature was also referred to. The literature indicated that the thermal decomposition temperature of the precursor was significantly higher than the test temperature. This, in addition to an examination of the structure and chemistry of the volatile species that were identified, gives us reason to believe that the volatile species are not thermal decomposition products of the precursor. As the stated purity of the precursor was greater than 98% (which leaves allowances for impurities), we reason that the volatile species that were detected were impurities.

We conclude that further examination of the overall propellant formulation process (including the individual components' synthesis processes) and process quality control (including purity of reagents and possible decomposition reactions) is indicated.

### Capabilities Provided

This work provides important data for further evaluations of green monopropellant vapor phase compositions. The experimental data suggests that the individual component tested has the potential to introduce volatile impurities into overall propellant formulation. Process evaluations are indicated that may result in reducing or eliminating volatile impurities in the final propellant. Propellant manufacturers, in cooperation with NASA, may use this work to evaluate and possibly



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improve green monopropellant formulations. A Joint Army-Navy-NASA-Air Force (JANNAF) report will be presented to the qualified propellant development and characterization community and the safety and industrial hygiene community after further studies have been completed.

## Potential Applications

Programs and projects (NASA, Department of Defense Agencies, commercial space entities, and industry) may use the results to gain a further understanding of volatile species characterization. Results disseminated to the propellant and safety community will increase awareness and help provide increased awareness of working with green monopropellant and promote improved techniques of formulation. If chemical inhibitors are added or processes for preparing the ingredients change, propellant specification changes will be recommended.

## Performance Metrics

Metric	Unit	Quantity
Test data	75	%